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The effect of input gas ratio on the growth behavior of chemical vapor deposited SiC films

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In an effort to protect a RBSC (reaction-bonded silicon carbide) reaction tube, SiC films were chemically vapor deposited on RBSC substrates. SiC films were prepared to investigate the effect of the input gas ratios (dilute ratio, $\alpha = P_{H2}/P_{MTS} = Q_{H2}/Q_{MTS}$) on the growth behavior using MTS (metyltrichlorosilane, CH_3SiCl_3) as a source in hydrogen atmosphere. The growth rate of SiC films increased and then decreased with the decrease of the input gas ratio at the deposition temperature of 1250°C. The microstructure and preferred orientation of SiC films were changed with the input gas ratio; Granular type grain structure exhibited the preferred orientation of (111) plane in the high input gas ratio region ($\alpha = 3$–10). Faceted columnar grain structure showed the preferred orientation of (220) plane at the low input gas ratios ($\alpha = 1$–2). The growth behavior of CVD SiC films with the input gas ratio was correlated with the change of the deposition mechanism from surface kinetics to mass transfer.

1. Introduction

Quartz glass tube has been commercially used in the integrated circuit (IC) industry for the furnace component [1]. SiO_2, Si_3N_4 and polycrystalline silicon films are deposited not only on the silicon wafers but also on the inside wall of reaction tube in the IC fabrication. As the deposits thicken, the difference of thermal expansion coefficients between the deposits and quartz glass tube caused the crack and flake of the deposits. The cleaning process for removing flake leads to inventory costs. From the last several years, SiC tube has been proposed as a replacement for quartz glass tube. SiC tube can reduce the crack and flake of the films on the inside wall of reaction tube by the compressive thermal stress of the deposits on SiC due to a significantly higher thermal expansion coefficient of SiC (4.4×10^{-6}) than quartz glass (5.0×10^{-7}). SiC has also an excellent property in chemical behavior such as oxidation, corrosion and creep resistance at high temperatures as well as in mechanical behavior [2–4].

RBSC (reaction-bonded silicon carbide) by the infiltration of the Si melt has been applied to reaction tube since it has little shrinkage after sintering. RBSC as a reaction tube has two problems at elevated temperatures. One is that residual Si on the surface of RBSC makes a reaction with the deposits because RBSC is actually composed of roughly 85% SiC and 15% residual Si [1, 5]. The other is that high purity condition of the furnace is hampered by the diffusion of impurities in RBSC. To solve these problems, SiC film having high purity is coated on the inside wall of RBSC tube for protective and diffusion barrier layer. SiC films from CVD (chemical vapor deposition) have advantages of good uniformity [6, 7], high purity, and stoichiometric composition. CVD SiC films with different microstructure in multi layer make diffusion of impurities difficult by increasing diffusion pass of impurities. The microstructure of CVD SiC films has relationship with deposition parameters such as the deposition temperature, total pressure, and the input gas ratio [4, 8–12]. In order to fabricate multi layer with different microstructure, to control total pressure or the input gas ratio as a deposition parameter offers more productivity and cost advantages than deposition temperature [13]. Most of researches on the microstructure [3, 4, 8–12, 14–16] have been focused on the effect of deposition temperature, not on the impact of total pressure and the input gas ratio.

In the present work, SiC films grown on RBSC substrates using MTS (metyltrichlorosilane) and hydrogen are investigated. The purpose of this work is to explain the influence of input gas ratio on the growth behavior as well as on the microstructure of SiC films. A second goal is to find the optimum condition for multi layer

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coating with different microstructure by manipulating the input gas ratio.

2. Experimental details

The experiments were performed in a horizontal hot wall reactor with a concentric double-tube structure, which are composed of an alumina tube on the outside and a mullite tube on the inside. The deposition apparatus was reported in a previous work [13]. MTS was chosen as a source precursor and hydrogen was used as both carrier and dilute gas. RBSC was used as a substrate, which was fabricated by a continuous reaction sintering process with α-SiC/graphite preform. The molten Si supplied from molten Si pool was infiltrated into α-SiC/graphite preform and dissolved graphite. Shortly after molten Si infiltration, β-SiC formed on the surface of graphite. The details of the RBSC fabrication process were reported in Park *et al.*'s work [5]. The deposits were prepared under the following conditions; Input gas ratios (dilute ratio, $\alpha = P_{H2}/P_{MTS} = Q_{H2}/Q_{MTS}$) ranged from 1 to 10 at the deposition temperature of 1250°C. Deposition temperatures ranged from 1050°C to 1300°C at the input gas ratios of 1, 4, and 8, respectively. Total pressure, MTS flow, and deposition time were fixed at 10 torr, 100 sccm, and 1 hour each.

The growth rate of SiC films was estimated by measuring the weight gain during deposition. The microstructure of SiC films was observed by SEM (scanning electron microscopy) and TEM (transmission electron microscopy). The crystal structure was characterized by X-ray diffractometer.

3. Results and discussion

Fig. 1 shows the variation of the growth rate as a function of the input gas ratio at the deposition temperature of 1250°C. As shown in Fig. 1, the growth rate is divided into two linear regions. In the higher input gas ratio region ($\alpha = 3$–10), the growth rate increased with the decrease of the input gas ratio. Going to the low input gas ratios ($\alpha = 1$–2), the growth rate decreased with the input gas ratio. In general, the growth rate is directly proportional to the MTS concentration [17, 18]. The result of the growth rate in the higher input gas ratio region is in good agreement with literatures [17, 18] because the MTS concentration increases with the decrease of the input gas ratio. But in case of the low input gas ratios, the tendency of the growth rate is different from that in the higher input gas ratio region. To interpret this discrepancy, we investigated the deposition mechanism of both the higher and low input gas ratios. Fig. 2 shows the Arrhenius plots of CVD SiC films at various input gas ratios. The variation of the growth rate depends on the deposition temperature and the input gas ratio. The growth rate rapidly increased with the deposition temperature in the low temperature region and saturated in the higher temperature region. The deposition mechanism is controlled by the surface kinetics in the low temperature region, whereas that is controlled by the mass transfer in the higher temperature region [19, 20]. The transition temperature of the deposition mechanism changed with the input gas ratio from about 1150°C for $\alpha = 1$ to about 1250°C for $\alpha = 4$. At $\alpha = 8$, the transition temperature of the deposition mechanism was estimated over 1300°C. At the deposition temperature of 1250°C, the deposition mechanism of $\alpha = 1$ and $\alpha = 8$ is controlled by mass transfer and surface kinetics, respectively.

The change of the deposition mechanism as shown in Fig. 2 is correlated with the variation of the growth rate as shown in Fig. 1. The deposition mechanism is controlled by the surface kinetics in the higher input gas ratio region ($\alpha = 3$–10). So *et al.* [10] reported that the growth rate increases with the MTS concentration in the surface kinetics regime. As the MTS concentration increases, the growth rate increases due to the increase of the intermediate reactive species bearing carbon and silicon from the homogeneous decomposition of MTS. Therefore, the deposition rate is directly proportional

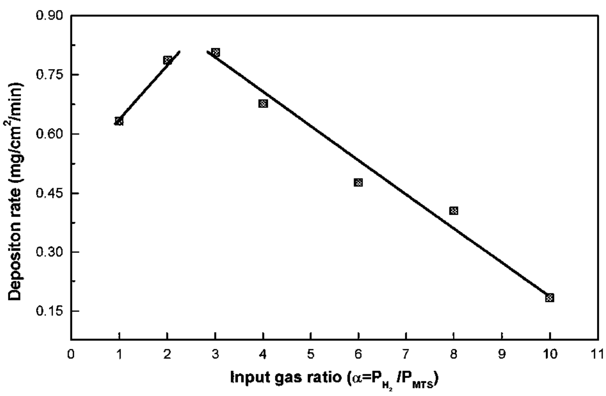

Figure 1 The variation of the growth rate as a function of the input gas ratio at $T = 1250$°C and $P = 10$ torr.

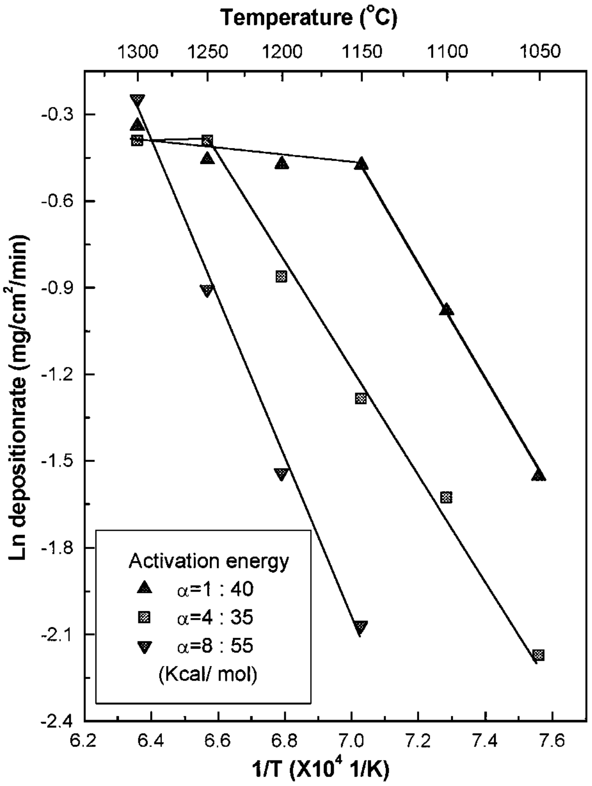

Figure 2 Arrhenius plots of CVD SiC films at various input gas ratios and $P = 10$ torr.

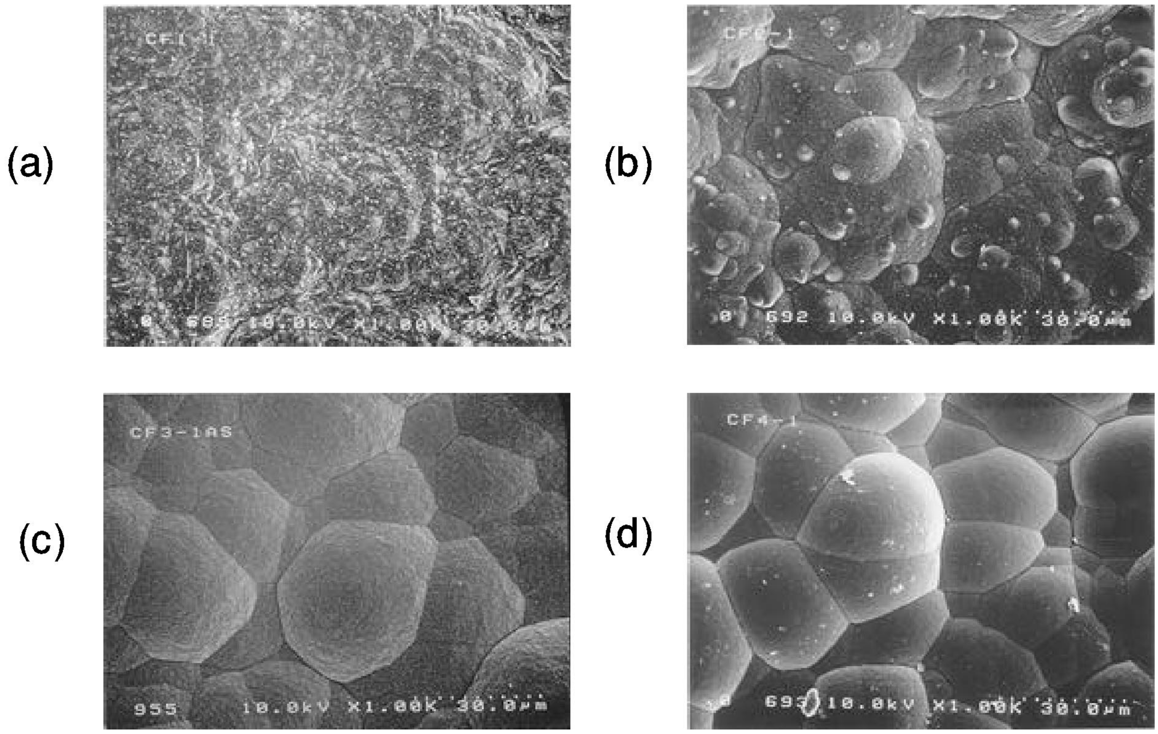

Figure 3 Plan view SEM image of SiC films as a function of input gas ratio at $T = 1250°C$ and $P = 10$ torr. (a) $\alpha = 1$, (b) $\alpha = 2$, (c) $\alpha = 3$, and (d) $\alpha = 4$.

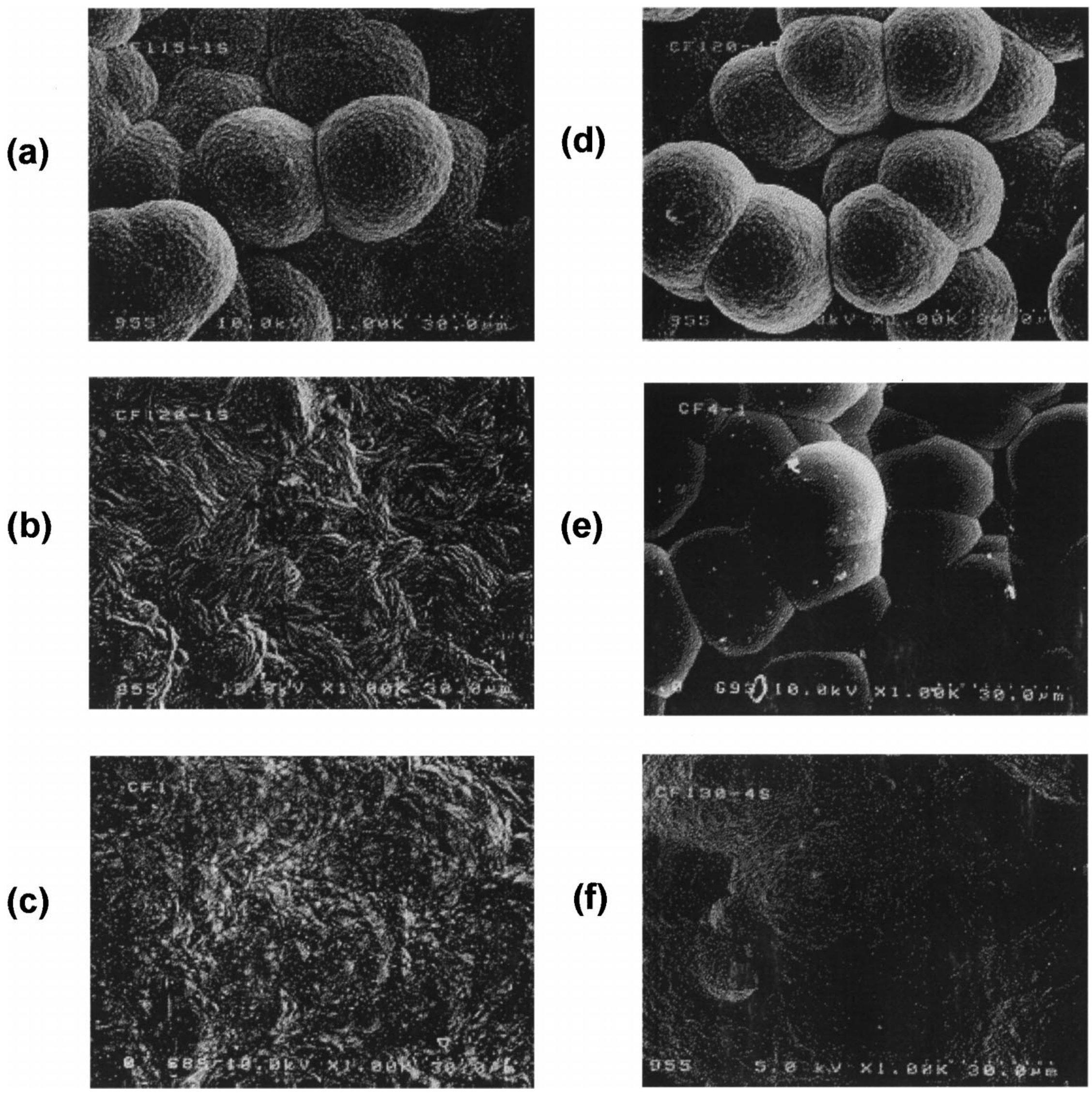

Figure 4 Plan view SEM image of SiC films with the deposition temperature in two series of the input gas ratio ((a), (b), (c) $\alpha = 1$ and (d), (e), (f) $\alpha = 4$) and constant total pressure of 10 torr. (a) 1150°C, (b), (d) 1200°C, (c), (e) 1250°C, and (f) 1300°C.

to the MTS concentration. Going to the low input gas ratios ($\alpha = 1$–2), or the higher MTS concentrations, the deposition mechanism is controlled by the mass transfer. From the kinetic study of Loumagne *et al*. [20], it is predicted that the input gas ratio also changes the deposition mechanism at the certain critical temperature and pressure. In the mass transfer regime, the gaseous diffusion of reactive species through a boundary layer is important [4]. The boundary layer is defined as the region near the substrate surface where the gas stream velocity, the concentration of the vapor species and the temperature are not equal to those in the main gas stream. Since the boundary layer thickness increases with the increase of temperature and the decrease of total pressure [19], the deposition mechanism with the increase of temperature is changed from the surface kinetics to the mass transfer. From the change of the deposition mechanism with the input gas ratio, it can be considered that the boundary layer thickness also increases with the decrease of the input gas ratio. The boundary layer thickness has a strong effect on the variation of the growth rate in the mass transfer regime. Therefore, the growth rate at the low input gas ratios decreases by decreasing the input gas ratio because of the increase of the boundary layer thickness. To confirm the relationship between the input gas ratio and the deposition mechanism, we observed the microstructure of SiC films with the input gas ratio and the deposition temperature.

Fig. 3 shows plan view SEM images as a function of the input gas ratio at the deposition temperature of 1250°C. The microstructure of SiC films was changed from the hemispherical granular type structure to the faceted columnar structure by decreasing the input gas ratio. The surface morphology of SiC films with the deposition temperature shown in Fig. 4 was also changed from the hemispherical granular type structure to the faceted columnar structure with the increase

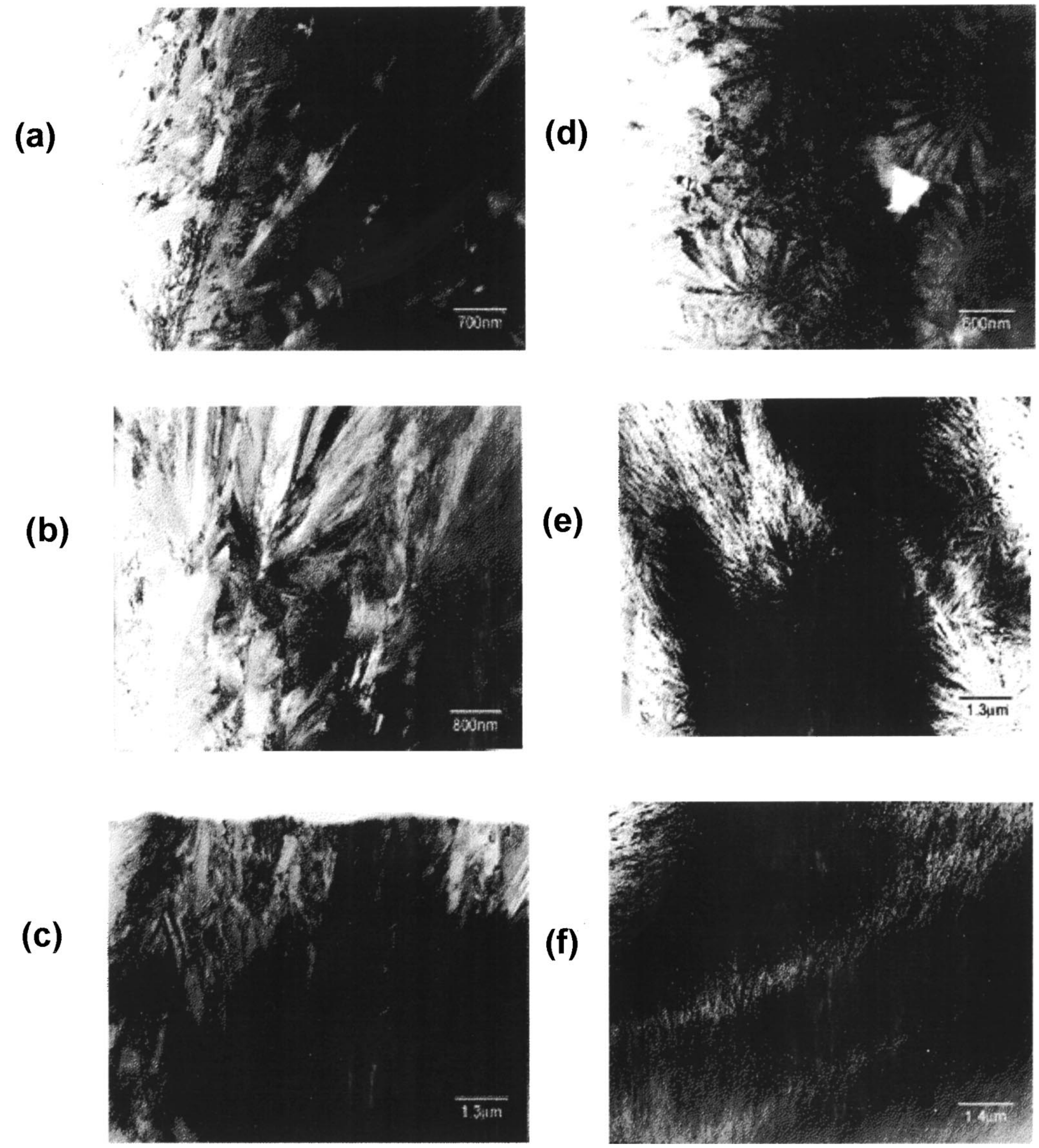

Figure 5 Cross-sectional view bright field TEM images of SiC films in two series of the input gas ratio ((a), (b), (c) $\alpha = 1$ and (d), (e), (f) $\alpha = 4$) at $T = 1250$°C and $P = 10$ torr. (a), (d) bottom region, (b), (e) middle region, and (c), (f) top region.

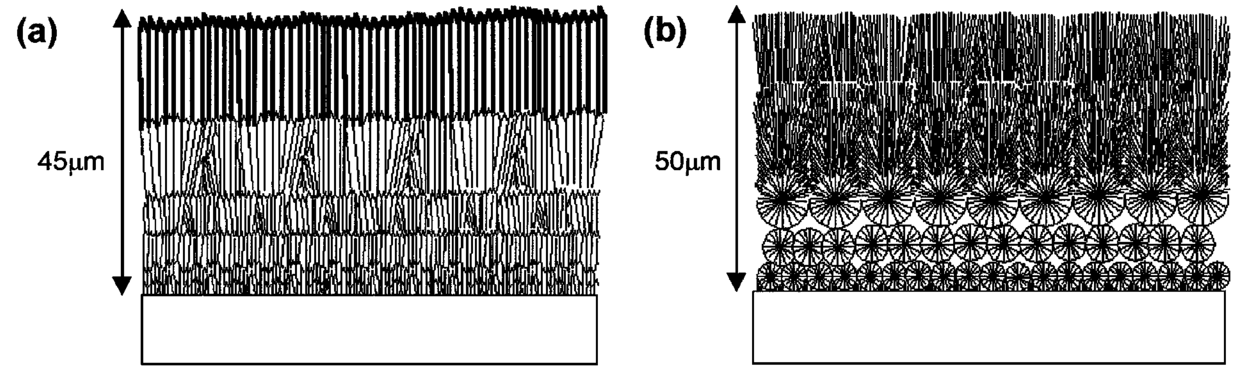

Figure 6 Schematic illustration of the microstructure from the cross-sectional TEM image at $T = 1250°C$ and $P = 10$ torr. (a) $\alpha = 1$ and (b) $\alpha = 4$.

of the deposition temperature. The transition temperature of the microstructure was slightly higher than that of the deposition mechanism in both case of $\alpha = 1$ and $\alpha = 4$. The microstructure of SiC films by CVD process strongly depends on the deposition temperature and mechanism [3, 12, 14]. In general, the mass transfer regime shows larger faceted columnar grains and the surface kinetics produced stratified textures and fine grain sizes. In the mass transfer regime, the mobility and the diffusion of reactive species are important [12]. The faceted columnar grain structure is formed in the mass transfer regime because reactive species find stable growth sites such as re-entrant edges and steps. In the surface kinetics regime, the microstructure of the films have the uniform nucleation and stratified textures due to the small mobility of adsorbed atoms on the surface. Therefore, the change of the microstructure with the input gas ratio is related with the deposition mechanism.

TEM was used to confirm the microstructure of a faceted structure and a granular type structure. Figs 5 and 6 show the cross-sectional TEM images and the schematic illustration of as-grown SiC films, respectively. The faceted columnar structure having the twin planes appears at $\alpha = 1$ (Fig. 5a, b, and c). The twin planes are formed from the stacking fault of β-SiC. The stacking fault occurs when two nuclei coalesce and rotate into precise twin relationship [3]. The spherical granular type structure which consists of fine grains shows the stratification structure near the substrate at $\alpha = 4$ (Fig. 5d). As films thicken, the microstructure of SiC films is changed from the spherical grain growth (Fig. 5d) to the radial grain growth (Fig. 5f). This variation of the growth mode at $\alpha = 4$ is not clearly understood yet but will be discussed in the further work.

X-ray diffraction analysis was performed to determine the crystalline phase and preferred orientation of films. The diffraction planes of β-SiC, i.e., (111), (220) and (311) planes, were obtained in the films deposited at the deposition temperature of 1250°C. Preferred orientation was estimated by texture coefficient (*TC* (*hkl*)) using the Harris method [21]:

$$TC\,(hkl) = \frac{I_{(hkl)}/I_{O(hkl)}}{\frac{1}{N}\sum\left[I_{(hkl)}/I_{O(hkl)}\right]} \qquad (1)$$

where, $I_{(hkl)}$, $I_{O(hkl)}$, and N are the measured intensities of the films, the standard intensities (from JCPDS file) of powdered SiC, and the number of reflections, respectively. The variation of the texture coefficient with the input gas ratio is shown in Fig. 7. The texture of films was the preferred orientation of the (111) plane in the higher input gas ratio region, whereas the preferred orientation of the (220) plane increased at $\alpha = 1$. The microstructure of the films affects on the preferred orientation of the films. Kim [16] reported that the development of a (220) preferred orientation is correlated with the formation of a faceted structure. Such phenomenon was also shown in our experiment. Consequently, the variation of the input gas ratio at the certain temperature as well as the variation of the deposition temperature induces the transitions of the microstructure and the preferred orientation.

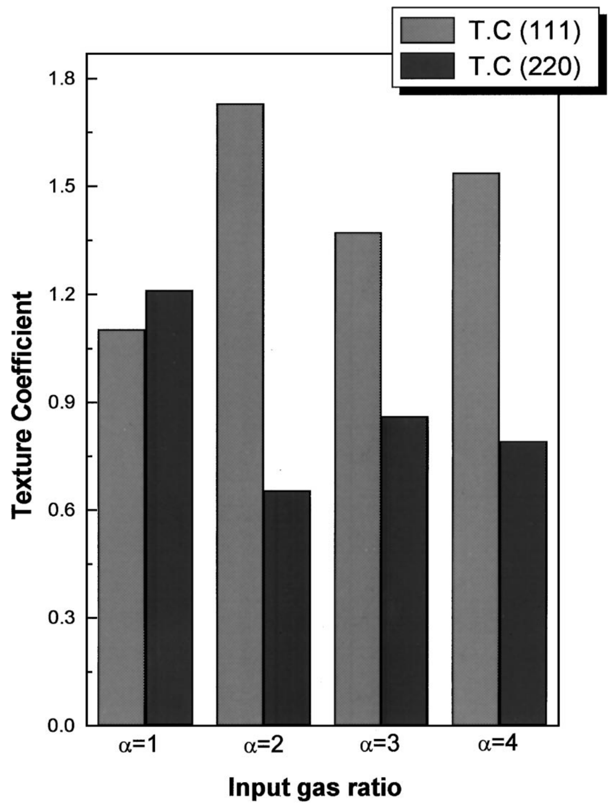

Figure 7 Comparison of texture coefficient with the input gas ratio at $T = 1250°C$ and $P = 10$ torr.

4. Conclusion

SiC films prepared by changing the input gas ratio showed the variation of the growth behavior that was correlated with the deposition mechanism. As the input gas ratio decreased at 1250°C, the growth rate increased in the higher input gas ratio region ($\alpha = 3$–10), but the growth rate decreased at the lower input gas ratios ($\alpha = 1$–2). In the higher input gas ratio region, the deposition mechanism is controlled by surface kinetics. At the lower input gas ratios, mass transfer through the boundary layer affected to the growth rate. The change of the deposition mechanism from surface kinetics to mass transfer also had an effect on the change of microstructure and texture from the granular type structure showing the preferred orientation of the (111) plane to the faceted columnar structure showing the texture of (220) plane.

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